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Instrumental Neutron Activation Analysis (INAA) of Beach Rock Samples of Andaman Island, India

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Abstract : Beach rock formation is a peculiar formation when compared to other rock formations. One such formation is found in Andaman Island, India and it needs intensive and extensive investigations. Elemental composition of beach rock samples collected from Andaman Island, India is determined using single comparator method of INAA. The collected samples were irradiated at thermal neutron flux of $10^{11} cm^{-2} s^{-1}$ at 20kw power using Kalpakkam mini reactor (KAMANI), IGCAR, Kalpakkam, Tamilnadu, India. Totally 8 elements have been determined from five samples using high resolution gamma ray spectrometry. The accuracy and precision were evaluated by assaying the irradiation and standard Reference material (Soil-5) and were found to be good agreement with certified values. Results are discussed and the conclusion is drawn.

Key words : Beach rock, Instrumental neutron activation analysis, Multi-Elemental Analysis.

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1. Introduction

Earth's crust is made up of various types of rocks. Beach rock is some peculiar type of rock. Beach rock, most commonly appearing as layered deposit inclined towards the sea, is a sedimentary formation indurated by the effects of carbonate cement-aragonite or magnesium calcite initially-formed in the intertidal zone. Like the beach itself, it represents a transition between the marine and meteoric environments, where it is commonly affected by processes from each environment.

Beach rock forms most commonly on beaches composed of calcareous shell and coral grains, but it can also develop in beaches of quartz sand or other mineral composition. It forms best on sand beaches; shingle or conglomeratic beach rock is less abundant. The natural factor of the beach, such as gentle slope of the foreshore, sufficient shell content and ground water temperature have also favoured the formation of beach rocks. Essential to beach rock development is ground water with enough calcium to provide cementing agent.

Such a beach rocks vary in color from pale yellowish orange, olive black, pinkish gray, moderate brown to pale reddish brown. Variation in color is mainly due to the admixture of white shell fragments and dark pebbles. An exposed beach rock is usually broken into rough rectangular blanks.This type of beach rock samples are found in many places in the world. One such beach rock formation is found in three (Wandoor, Neill Island and Chidyatapu) different beaches of Andaman island, India. A number of modern non-destructive techniques which are rapid highly sensitive and require a small amount of samples, have been commonly used for elemental analysis; electron scattering for chemical analysis (ESCA), X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA). Neutron activation analysis is one of the most powerful and widely used techniques based on the use of radioactivity in elemental analysis. With the advent of nuclear reactors, NAA soon became a very useful tool in trace analysis. For many years NAA was in fact the only means of studying many elements present

at low concentration levels in materials such as silicate rocks, meteorites, high purity metals and biological tissues.

In present study beach rock samples were collected at three different locations of Andaman Island, India and elemental composition of beach rock samples were determined in qualitative and quantitative using instrumental neutron activation analysis (INAA).

2. Materials and Methods

2.1. Sample Collection and Preparation

The samples were collected at three locations (Wandoor-B1-B2), (Neill Island- B3-B4), (Chidyatapu-B5) using global positioning system (QueM5 with accuracy: up to 10m). A detailed geological survey was carried out before the fieldwork. At these localities the samples were collected along the tide line i.e. along the horizontal transect. In each location 1 to 2 samples of 2 kg bulk of beach rock samples were collected in a polythene bags. All the samples were cleaned, weathered surface removed and the remaining fresh materials crushed into small pieces. These samples are powdered using agate mortar and dried for 24 hrs at a temperature of 110°C and then pulverized to particle sizes not greater than 2mm mesh screen. The typical beach rocks are shown in Figure1 and Figure 2.

Figure 1. Beach rocks of Wandoor (B1)

Figure 2. Beach rocks of Chidayatapu (B5)

2.2. Sample Irradiation and Counting

Irradiations were performed in thermal neutron flux of using pneumatic transport facility of KAMANI research reactor, Kalpakkam. To determine the long lived radionuclides (^{153}Sm, ^{140}La,^{76}As,^{46}Sc,^{60}Co,^{152}Eu and ^{59}Fe) in beach rock samples, all samples were irradiated in reactor by 6 hours. They were counted for 10,000-30,000s after cooling time of 2,4to7 and 35 to 50 days. Data acquisition in all these cases was done using a PC based MCA, coupled to vertical HPGe detector system.

2.3. Radioactive Assay

After irradiation the polypropylene tubes containing the sample and the gold as the standard for quantitative analysis were washed under running water, wiped and mounted on standard Perspex plates. Samples were assayed for g- activity of the activation products using an 80 cm^3 HPGe detector coupled to a PC based 4K analyzer in an efficiency calibrated position with reproducible sample to detector geometry. The sample to detector distance was maintained at 12-15 cm depending upon the level of activity to avoid true coincidences effects. The

detector system had a resolution of 1.8 keV at 1332 keV. The activities of radionuclides were considered as a function of time to ensure purity and identity. Gamma-ray standard of ^{152}Eu was used for efficiency calibration of the detector, at different distances between the sample and detector in a stable source to detector geometry.

2.4. Calculations

Peak areas corresponding to different photo peaks, after subtracting the linear Compton background, were converted to specific count rate (*A*sp) by *A*sp=*P*A /*SDCW,* where *P*A=peak area, *S*=saturation factor, *C*=counting correction, *D*=decay correction, and *W*=weight of the sample.

The concentration of the ith element (in μg/g) was calculated by Conc=[*A*sp/(*A**sp*K*anal)], where *A*sp=specific countrate corrected per gram of the sample, *A**sp=specific count rate of ^{198}Au, and *K*anal = *K*0 [(*f* +*Q*0 (a))/(*f* +**Q* (a))]·(*ξ*/*ξ**), where *ξ* is the detection efficiency of the detector for the g-ray energy used, *f* is the sub-cadmium to epicadmium neutron flux ratio, and *Q*0(a) is the ratio of cross sections and is equal to *I*0(a)/sth, where *I*0(a) is the infinitely dilute resonance integral corrected for the non-ideal epithermal neutron flux distribution. Validation for the experimental setup was done by irradiating the Standard Reference Material (Soil-5) for the same period of time with comparator and the sample in the same location of the reactor (Table-1). The SRM analysis agreed well with the certified values.

3. Results and Discussion

3.1. INAA Analysis

The concentration of determined elements in beach rock samples of Andaman Island, India from 3 sampling sites are reported in Table-2. The samples were identified as B1, B2, B3,B4 and B5 in the ordering of sampling locations.

Calcium was found to be the most abundant element in beach rock samples. It plays a major role in the beach rock formation. It was found to be more dominant element than other elements in the present study. It varies from 22.36% to 29.03% with an average of 26.33%. The lowest and highest value of this element was recorded for B5 and B3 respectively. Variation of calcium in the samples may be thought of as being controlled by clay minerals. Nelson [7] has pointed out that in the processes of ion exchange the common ions inherited from soil environment (Ca^{2+} and H^{+}) by the absorption in surfaces particles are replaced by the most abundant ions (Na^{+} and Mg^{+}). The net reaction between fluvial clays and seawater is primarily an exchange of seawater Na for bound Ca [9,10]. The highest concentration of Ca in the samples may be due to the significant incorporation of clay sized $CaCo_3$ material in sediments [3].

It can be seen from Table 2 calcium is the most abundant element. In the present study, its concentration is about 4 times the crustal average value, but it is lower than the carbonate rocks. This may be due to typical beach rock formation [2, 4,5].

The concentration of iron varied from 0.16 to 1.49% with an average of 0.66%. It registered the lowest and highest values for B2 and B1 respectively. This may be due to iron being incorporated within calcite during primary precipitation of calcite in reducing condition and was the result of input and sedimentation rate of detrital mineral into the depositional environment[1].

Cobalt is among the most widely distributed heavy metals in terrestrial and aquatic environment. In natural sediments the distribution of cobalt is frequently related to that fine grain material, which is usually dominated by clay minerals. It could be seen from the Table 2, its concentration varies from 1.68 to 8.12 ppm with an average of 3.16 ppm. It was found that, the cobalt value in the present study is lower than crustal average but higher than carbonate. The lowest and

highest levels were recorded for B3 and B1 respectively. The low concentration of this element may be attributed to its mobility, which is reduced in the carbonate dominant environment [6]. The highest concentration of this element in the sample at B1 may be due to the flocculent nature of the sediments that might had changed the amount of metal deposited [8]. In general, the concentration of cobalt was found to be low in almost all sampling sites.

3.2. Rare Earth Elements (REEs)

Rare earth elements (REE, As, La, Sm, Sc and Eu) form a coherent group with very similar chemical properties. Because of these properties, the REE behaviour is important in revealing various chemical fractionation processes in geological and biological systems. In geological materials, REE provide characteristic fingerprint of different minerals that comprise a rock.

From Table 2 it could be seen that the average rare earth element of As, La, Sc, Sm and Eu in beach rock samples are 9.75, 2.80, 1.59, 0.80 and 0.36ppm respectively. In the Andman beach rock samples, the content of REEs follow the order As > La > Sc >Sm> Eu. This is comparable with the sequence of the average REE abundance order in Earth's crust [11].Generally, REEs have rather short residence time in oceans and relative enrichment in the heavier REE (HREE) is common in nature.

Element	Certified values	INAA values
Sm-153	5.42	5.04
La-140	28.10	27.01
As-76	93.90	84.57
Sc-46	14.80	15.34
Co-60	14.80	14.96
Eu-152	1.18	1.13
Fe-59 %	4.45	4.55

Table-1 Analysis of Standard Reference Material (Soil-5) by INAA
(in ppm unless % indicated)

Sample/ Element	Ca%	Fe-59 %	Sm-153	La-140	As-76	Sc-46	Co-60	Eu-152
B1	28.14	1.49	1.61	4.08	11.40	5.24	8.12	0.54
B2	25.67	0.16	0.43	1.86	3.90	0.44	2.28	0.25
B3	29.03	0.41	0.87	3.72	9.01	0.82	1.68	0.36
B4	26.45	0.69	0.61	2.51	13.81	0.81	1.95	0.37
B5	22.36	0.56	0.48	1.83	10.66	0.65	1.78	0.32
Average	**26.33**	**0.66**	**0.80**	**2.80**	**9.75**	**1.59**	**3.16**	**0.36**

Table 2-Elemental composition of beach rock samples of Anadaman island,India

(in ppm unless % indicated)

Conclusion

Based on the geochemical studies on beach rock samples by INAA, it is inferred that the cementation of beach rock is due to the calcium carbonate. There is high abundance of calcium carbonate in tropical and subtropical areas of ocean and also typical beach rock formation. The distribution of rare-earth elements (REE) also studied for petrogenic processes.

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